

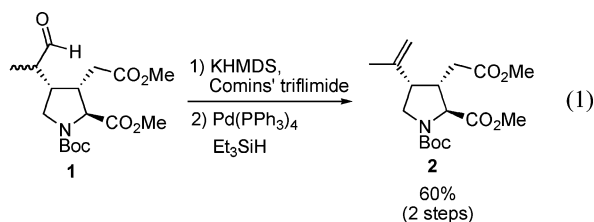
Terminal Olefins from Aldehydes through Enol Triflate Reduction

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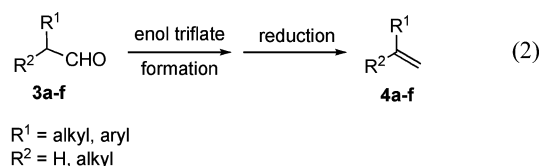
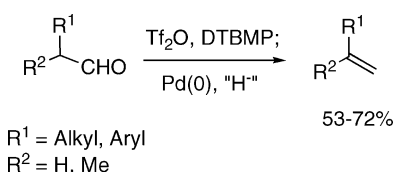
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Although olefins have frequently been prepared from ketones by reduction of the derived enol triflates,⁵ surprisingly, this strategy has never, to our knowledge, been previously applied to aldehydes. In this Note, it is shown that this aldehyde to olefin conversion is quite general and offers a useful alternative to existing approaches (eq 2).



The transformation of aldehydes into terminal olefins through reduction of the corresponding enol triflates is described. The method is effective with both linear and α -branched aldehydes.

In the course of our recent synthesis of kainic acid, we required an efficient procedure for converting a 1-formylethyl substituent into an isopropenyl group.¹ This type of olefination has often been achieved indirectly via the corresponding alcohol by using the Sharpless–Grieco methodology,² which involves oxidation–thermal decomposition of a derived selenide.³ While this approach is generally effective, it has at times proven unsatisfactory, most often with branched and oxidation-sensitive substrates,⁴ and indeed failed to yield an acceptable result in the context of our synthesis. Fortunately, it was discovered that olefin **2**, the penultimate intermediate in our sequence, could be cleanly secured from aldehyde **1** by reduction of the derived enol triflate (eq 1).

A number of aldehydes, linear and α -branched, were selected to test the breadth of this olefination procedure. The results are summarized in Table 1. The study began with the methylenedioxy derivative **3a**, which was used to define the optimum conditions for enol triflate formation and the subsequent reduction. The preparation of the enol triflate was first carried out through treatment of **3a** with potassium *tert*-butoxide in THF,⁶ followed by addition of the Comins reagent⁷ (2-[*N,N*-bis(trifluoromethylsulfonyl)amino]-5-chloropyridine). Reduction of the triflate (3:1 mixture) with Pd(OAc)₂(PPh₃)₂ and tributylammonium formate⁸ then produced olefin **4a** in 54% overall yield (method A, entry 1). Notably, no double bond isomerization to form the styryl derivative was observed. The reduction of the enol triflate with triethylsilane and Pd(PPh₃)₄ in DMF⁹ was also efficient, but olefin **4a** could not be obtained totally free of silicon contaminants. The reaction of aldehyde **3a** with triflic anhydride in conjunction with 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP)¹⁰ in 1,2-dichloroethane at 70 °C for 1 h also led to the formation of the enol triflate (ca. equimolar *E/Z* mixture, 66% isolated yield). The reduction of this triflate using Pd(OAc)₂(PPh₃)₂ and tributylammonium formate afforded again the expected olefin **4a** in 86% yield (method B, entry 2). While the overall yield (57%) proved just slightly higher than that obtained above, the approach is more economical and experimentally convenient. Both the overall yield and the convenience could be further improved by subjecting the crude triflate directly to reduction: the crude reaction product, obtained from **3a** by treatment with triflic anhydride and DTBMP, followed by simple filtration through a short plug of silica gel and removal

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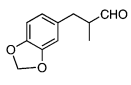
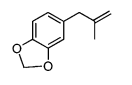


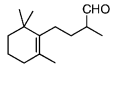
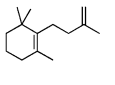




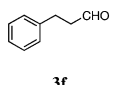

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TABLE 1. Conversion of Aldehydes to Olefins

Entry	Aldehyde	Method ^a	Product	Yield(%) ^b
1		A		54
2		B		57
3		C		63
4		C		64
5		A ^c		53
6		C		65
7		C		72
8		C		65 ^d

^a Method A: (i) *tert*-BuOK, Comins' reagent, THF; (ii) Pd(OAc)₂(PPh₃)₂, HCO₂H, NBu₃, DMF. Method B: (i) Tf₂O, DTBMP, CICH₂CH₂Cl; (ii) Pd(OAc)₂(PPh₃)₂, HCO₂H, NBu₃, DMF. Method C: same as B, but no triflate purification. ^b Overall yield. ^c Method C provided the olefin in ca. 85% purity. ^d Contains a small amount (<3%) of β -methylstyrene.

of volatiles, on reduction with Pd(OAc)₂(PPh₃)₂ and tributylammonium formate provided olefin **4a**, now in 63% yield (method C, entry 3). This simple and rapid protocol (triflate formation 1 h, reduction 0.5 h, no intermediate purification) was used, except for entry 5, with the other aldehydes in Table 1.

From the aliphatic α -branched aldehyde **3b**, the olefin **4b** was obtained in good yield, despite the volatility of the product (entry 4). With aldehyde **3c**, the olefin formed by using method C was inseparable from a small amount (ca. 15%) of a byproduct produced during enol triflate formation. In this case, application of method A allowed isolation of the pure diene **4c** in 53% overall yield (entry 5). α -Methylstyrene **4d** could be obtained with no sign of polymerization in 65% yield from the phenylacetaldehyde derivative **3d** (entry 6).

This olefination method, while probably more useful for the synthesis of disubstituted olefins, can also be applied to straight-chain aldehydes to produce linear alkenes. Dodecenal **3e**, for

example, could be converted in good yield into dodecene **4e** (entry 7). There was no double bond migration to an internal position under the reduction conditions, a phenomenon often encountered with palladium(II) catalysts.¹¹ Only when the reaction mixture was allowed to react for a longer time and/or at a higher temperature did the formation of double bond isomers occur. The olefin from aldehyde **3f** showed a greater propensity for double bond isomerization; however, reduction of the crude triflate with the palladium catalyst and tributylammonium formate at 35 °C for 30 min afforded the unconjugated olefin **4f** in 65% yield with less than 3% isomerized product (entry 8).

The case of kainic acid (eq 1) is interesting in that the aldehyde precursor **1** bears multiple functional groups. Triflic anhydride and DTBMP did not cleanly produce the intermediate enol triflate, most likely due to incompatibility with the *N*-Boc protecting group.¹² The use of KHMDS and Comins' reagent, however, led to clean formation of the enol triflate in the presence of the Boc and two methoxycarbonyl groups. The reduction of the triflate could, in this case, be carried out with triethylsilane as the hydride source due to the relatively polar nature of the product.

In conclusion, a simple method that permits rapid transformation of an aldehyde, branched or linear, into a terminal alkene has been developed. The method proceeds in useful yields, is comparatively economical, and avoids the use of toxic selenium derivatives.

Experimental Section

General experimental procedure, method C: To a stirred solution of aldehyde **3** (1.0 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (1.2 mmol) in 1,2-dichloroethane (4.0 mL) under argon is added triflic anhydride (1.1 mmol), and the resulting solution is heated at 70 °C for 1 h. After being allowed to cool to room temperature, the reaction mixture is filtered through a short plug of silica gel, the filtrate is concentrated under reduced pressure, and DMF (2.0 mL), Pd(OAc)₂(PPh₃)₂ (0.05 mmol), NBu₃ (3.0 mmol), and formic acid (2.0 mmol) are added. The reaction mixture is stirred at 35 °C for approximately 30 min and then processed in the usual way, and the crude reaction product is purified by flash chromatography on silica gel to provide olefin **4**.

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Supporting Information Available: Characterization data and ¹H and ¹³C NMR spectra for compounds (**4a–f**); experimental procedures for methods A and B. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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